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Synthesis and Structural Characterization of Cr(III) Complex of Porphyrazine and Phthalocyanine Derivatives: Kinetic Studies of Metalation and Redox Activity

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Chromium(III) complexes of 2,3,7,8,12,13,17,18-*octakis*(propyl)porphyrazine and 2,3,9,10,16,17,23,24-octa substituted phthalocyanine were synthesized, characterized and the kinetics of metalation and redox activity studied and reported. The results obtained indicated that the rate of incorporation of Cr(III) into the central cavity of the ligands is a function of the kinetic inertness and size of the metal ion as well as the peripheral substituents of the ligand. The Cr(III) complex of 2,3,7,8,12,13,17,18-*octakis*(propyl)porphyrazine exhibited a metal based reduction. Hence it was concluded that the nature of the incorporated metal ions has an influence on the rate and mechanism of incorporation of the metal ion and also the redox activities of these complexes.

Keywords: Chromium(III), Complex, Porphyrazine, Phthalocyanine, Kinetics.

INTRODUCTION

Tetrapyrrole macrocyclic complexes have received immense interest in recent years because of their biological relevance and their technological applications are very broad [1-3]. They exhibit unique redox performance as a result of their accessible π and π^* orbitals, which allows at least partial oxidation or reduction of the macrocycle [4-10]. They are therefore used as electro-catalysts for heterogeneous and homogeneous chemical reactions, sensors as well as semiconductors [1,3,9,10]. Their redox activities may be metal or ligand based [9] and the incorporated metal ions either redox-active or -inactive [1-3,9,11,12]. Generally for complexes with incorporated redox-active metal ions, metal based redox processes occur first [1-3,9,11,12]. Their redox activity may be tuned by the modulation of their peripheral substituents and the incorporation of various metals ions within their central cavity [1]. An investigation of the kinetics of the incorporation and redox activities of these complexes may therefore be vital towards the enhancement of their applications.

Previous studies on these complexes had primarily focused on their syntheses, characterization and electrochemistry using divalent metal ions [1-3,9,11]. Few studies had been carried out on the kinetics of metalation and the redox activities of these macrocycles with trivalent transition metals ions [2,12]. The kinetics of the redox activities of some tetrapyrrole macrocyclic complexes with redox-inactive divalent metal ions had been studied and these exhibited a ligand based process [13]. In an effort to provide evidence for metal-based redox process and probable mechanism of incorporation for trivalent metal ions, it was suggested that an investigation of the redox process involving complexes of similar ligands with a redox-active trivalent metal ion may be carried out using Cr(III). Hence the objective of this work was to synthesize chromium(III) complexes of 2,3,7,8,12,13,17,18-*octakis*(propyl)porphyrazine (**1a**) and 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (**2a**), their characterization and study the kinetics of metalation and their redox reactions.

EXPERIMENTAL

All the solvents used were purified according to standard literature techniques and the reactions were done under nitrogen atmosphere. Flash column chromatography was carried out on Merck Kieselgel 60 (230-400 mesh) under nitrogen pressure. Thin layer chromatography was performed using Merck 60 F_{254} silica gel sheets. NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer in $CDCl_3$. Electronic spectra were measured on a Varian Cary 50 ultraviolet-visible spectrophotometer, using a matched pair of 1 cm path length quartz cuvettes, measurements were made from 300 nm to 800 nm. Infrared spectra was recorded on a Nicolet 410 impact Fourier transform infrared spectrophotometer using nujol or potassium bromide cell, in the range 4000 and 500 cm^{-1}. The synthesis

of the complexes of the ligands was carried out by established methods as described [9]. Compounds **3-7** and **8-9** were prepared according to published procedures [9,12].

Syntheses of ligands

Synthesis of 2,3,7,8,12,13,17,18-*octakis*(propyl)-porphyrazinato magnesium(II) (1c): Compound **1c** was prepared according to the established method (**Scheme-I**) [12]. Butanol (20 mL), magnesium (77 mg, 3.17 mmol) and iodine crystals were refluxed for 24 h after which 2,3-dipropylmaleonitrile, **6** (300 mg, 0.831 mmol) was added to the suspension of magnesium butoxide and the reaction mixture refluxed for 24 h away from direct light. The brownish purple solution obtained was evaporated and the residue was re-dissolved in ethyl acetate. It was then purified using flash column chromatography with ethyl acetate: dichloromethane (1:10) solvent system.

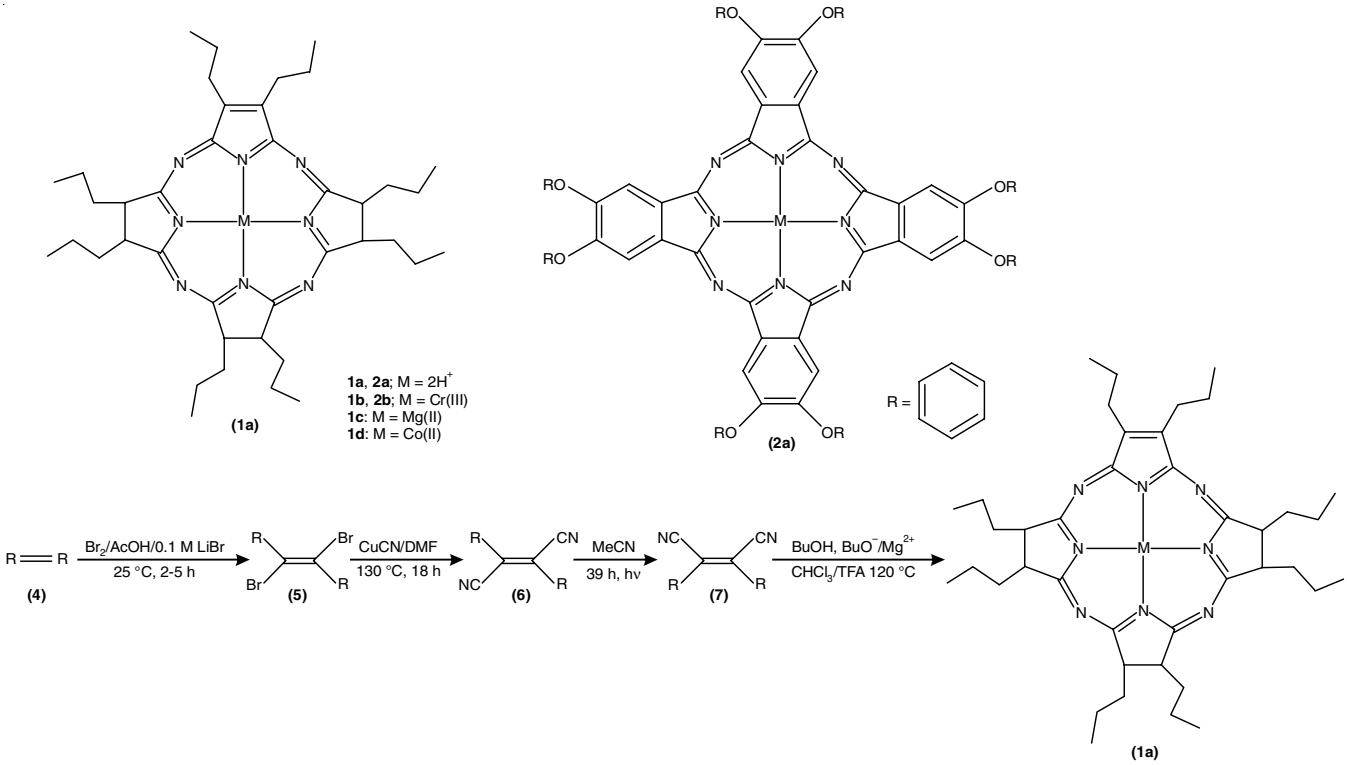
Yield about 92 mg, 0.136 mol; Yield (%) 4.3; R_f = 0.61, ethyl acetate:dichloromethane (1:10). IR (KBr, ν_{max}, cm^{-1}): 3021 (C-H) aromatic, 2928-2851 (CH_2, CH_3), 1643 (C=C), 1379 (C-H), 470 (N-Mg). UV-visible λ_{max} (nm): 345, 550, 600. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, 24H, *J* = 7.5 Hz), 2.52 (hp, 16H, *J* = 7.4 Hz), 4.06 (t, 16H, *J* = 7.5 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 15.20, 26.22, 28.84, 30.08, 30.59, 122.78, 123.17, 123.50, 123.83, 134.81, 135.17, 135.50, 135.82, 143.92, 149.47, 149.83, 150.19, 158.82. Anal. calcd. C, 68.05; H, 7.31; N, 19.30. Found: C, 68.93; H, 7.28; N, 20.00.

Synthesis of 2,3,7,8,12,13,17,18-*octakis*(propyl)-porphyrazine (1a): Removal of magnesium from **1c** (0.58 g) was accomplished by heating it at reflux in a $CHCl_3$/TFA (20:1) solution (200 mL), which was made basic by the addition of NaOH. The organic layer was separated, washed once with 10 % aqueous NaOH (50 mL) anhydrous Na_2SO_4 and filtered. Compound **1a** was adsorbed onto a silica gel, column chromatographed and eluted with CH_2Cl_2/hexane (1:1). Slow evaporation of the solvent gave a microcrystalline solid, which was recrystallized by slow diffusion of benzene into a $CHCl_3$ solution of the **1a** base Yield = 0.48 g, % Yield = 0.827, R_f = 0.413 (hexane: ethyl acetate, 10:1). (KBr, ν_{max}, cm^{-1}): 3395 (N-H), 2928-2851 (CH_2, CH_3), 1209 (C=C), 723 (C-H). UV-visible λ_{max} (nm): 339, 558, 626. ^{1}H NMR ($CDCl_3$) δ = -2.11 (s, 2H, NH), 1.86 (t, 24H, *J* = 7.7 Hz, CH_3), 3.98 (ν 16H, *J* = 7.7 Hz, $\underline{CH_2}CH_2CH_3$). Anal. calcd. C, 71.74; H, 7.97; N, 20.29. Found: C, 71.68; H, 8.01; N, 20.28.

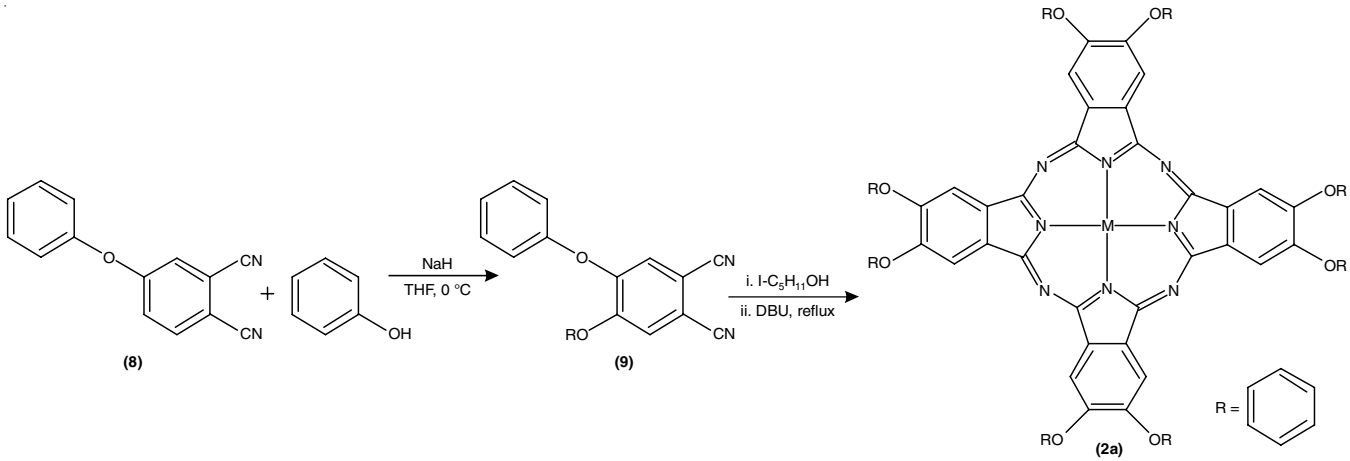
Synthesis of 2,3,9,10,16,17,23,24-octa substituted phthalocyanine (2a): To NaH (0.15 g) and phenol, (0.353 g, 0.0375 mol) in THF (15 mL) was added and 4-nitrophthalonitrile (0.50 g, 0.0028 mol), in THF (15 mL) and refluxed for 8 h. The resulting 1,2-diisocyano-4-phenoxybenzene (**8**) was filtrated and the solid washed with ethyl acetate and both the filtrate and the washing were mixed and evaporated under reduced pressure (**Scheme-II**). The resulting white precipitate was purified by flash column chromatography using solvent system, ethyl acetate:hexane (1:4). Yield = 0.737 g, % Yield = 86.4, R_f = 0.36 (ethyl acetate:hexane, 1:4).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (s, 2H), 3.46 (m, 5H, CH) 7.07 (m, 3H, ArH), ^{13}C NMR (300 MHz, $CDCl_3$) δ 71.01, 117.45, 119.69, 119.92, 126.95, 127.34, 134.43, 135.20.

1,2-Diisocyano-4-phenoxy benzene (**8**) (0.300 g, 1.36 × 10^{-3} mol) and phenol (0.356 g, 0.0375 mol) in THF was refluxed. The resultant product (**9**), 1,2-diisocyano-3,4-diphenoxy benzene, (0.300 g, 1.36 × 10^{-3} mol) was refluxed in 1-pentanol (14 mL) and 1 mol 1,8-diazabicyclo[5.4.0]-undec-7-ene (0.21 g, 1.36 × 10^{-3} mol) for 16 h. Methanol (20 mL) was there after added and the precipitate (**2a**) filtered off, Soxhlet extracted with methanol and acetone and dried at 60 °C. Yield = 0.294 g and



Scheme-I: Synthesis of 2,3,7,8,12,13,17,18-*octakis*(propyl)porphyrazine (**1a**)



Scheme-II: 2,3,9,10,16,17,23,24-Octa substituted phthalocyanine (**2a**)

yield (%) 43, R_f = 0.23 (ethyl acetate:hexane, 3:8). (KBr, ν_{max}, cm^{-1}): 3620 (N-H), 2848 (C-H) aromatic, 1685 (C=C), 1163 (C-H), 743 (C-H). UV-visible λ_{max} (nm): 337, 606, 640, 661, 702. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 2H, NH), 3.66 (m, 4H, CH), 6.99 (m, 4H, ArH), 7.23 (m, 4H, ArH), 7.50 (m, 4H, ArH) 8.04 (m, 4H, ArH), 8.99 (m, 4H, ArH), 9.23 (m, 4H, ArH), ^{13}C NMR (300 MHz, $CDCl_3$) δ 71.01, 76.57, 76.99, 77.41, 117.45, 119.69, 119.92, 126.95, 127.48, 127.63, 128.53, 128.85, 128.94, 134.43, 135.20. Anal. calcd. C, 76.21; H, 4.19; N, 9.03. Found: C, 76.21; H, 4.18; N, 9.11.

Syntheses of complexes: The complexes were prepared according to the modification of established methods [14,15]. Chromium(III) chloride hexahydrate (0.20 g, 0.001 mol) was dissolved in ethanol and stirred until a clear solution was obtained. This was added to a solution of the free base ligands **1a** (0.65 g, 0.001 mol) and **2a** (1.15 g, 0.001 mol) in dichloromethane with stirring until a uniform solution was attained. This mixture was heated for 0.5 h under nitrogen controlled environment. The product thus obtained was allowed to cool, filtered and washed with chloroform. A dark green residue was obtained for both complexes which was recrystallized and washed with acetone-methanol mixture.

Compound 1b: Yield about 3.58 g and yield (%) = 51.12; (KBr, ν_{max}, cm^{-1}): 3012-2935 (C-H), 1329 (C-N) 1153 (C-H), 550 (Cr-N); UV-visible λ_{max} (nm): 333, 462, 557, 625. Anal. calcd. C, 79.43; H, 4.63; N, 9.92. Found: C, 79.54; H, 4.71; N, 9.98.

Compound 2b: Yield about 5.37 g and yield (%) = 44.71; (KBr, ν_{max}, cm^{-1}): 2851 (C-H) aromatic, 1661 (C=C), 1351 (C-N), 1158 (C-H), 561 (Cr-N); UV-visible λ_{max} (nm): 331, 460, 672, 710. Anal. calcd. C, 74.30; H, 4.19; N, 8.66. Found: C, 74.27; H, 4.23; N, 8.69.

Kinetic studies

Metalation: The reactions were monitored spectrophotometrically by a Varian Cary 50 ultraviolet-visible spectrophotometer with a thermostated cell compartment maintained at 25 ± 0.1 °C. Metalation of the ligands was carried out in 1 cm cells by mixing solutions of the ligands to solution of chromium(III) chloride hexahydrate, pre-equilibrated at the reaction temperature. The UV-visible absorption spectrum was scanned from 300 to 800 nm and readings were taken at constant wavelength. The absorption spectra changed as a function of time with distinct isosbestic points until completion of the reaction. The kinetics was run under pseudo-first order conditions with the metal ion concentration at a large excess over that of the corresponding free base ligand.

Redox: Solutions of **1b** in dichloromethane were allowed to equilibrate at 25 °C under nitrogen atmosphere. Solutions of **1d** in glacial acetic acid under nitrogen was also prepared and allowed to equilibrate at 25 °C. The solutions were mixed and quickly transferred to a 1 cm quartz cell in a thermostated compartment of the Cary 50 spectrophotometer. The UV-visible absorption spectrum from 300 to 800 nm was scanned and readings were taken. The absorption spectra changed as a function of time with distinct isosbestic points until completion of the reaction.

RESULTS AND DISCUSSION

The structure of the compounds was confirmed using elemental analysis, FTIR, ^{1}H NMR, ^{13}C NMR and UV-visible spectroscopic techniques. The elemental analysis results obtained are in close agreement with the calculated values. Spectral assignment of the compounds was achieved by the comparison of the spectra of the compounds with those of their starting material and that of similar compounds.

2,3,7,8,12,13,17,18-*octakis*(propyl)porphyrazine (1a): ^{1}H NMR spectrum of compound **1a** displayed a broad peak at 2.11 ppm diagnostic of the N-H protons in its inner core. Similar peaks have been reported to be indicative of the shielding of the pyrrolenine nitrogen atoms of porphyrazines [16,17]. Consequently confirming the formation of the macrocycle and hence the demetalation of **1c**. Evidence of the cyclotetramerization of the dinitrile was given by the absence of the C≡N band in this spectrum. This was however observed at 3.00 ppm in the spectrum of dipropylmalenitrile, **6**, one of the starting material [18]. A triplet observed at 1.86 ppm was assigned to the methyl protons of the propyl substituents. The triplet at 3.98 ppm corresponds to protons attached to carbon of the propyl substituent linked to the pyrrole rings $\underline{CH_2}CH_2CH_3$ [12]. The infrared spectrum of **1a** on the other hand showed a weak band at 3395 cm^{-1} indicative of the two protonated nitrogen atoms in the inner core of the porphyrazine ring, suggesting **1a** was metal free. This was further corroborated by the N-Mg stretching frequency in the spectrum of **1a**

observed at 470 cm^{-1} for **1c** [19]. The most revealing data for a tetrapyrrole macrocyclic system is given by its UV-visible spectra in solution [1]. Metal containing porphyrazines have D_{4h} symmetry consequently the Q band appears as one peak in the visible spectrum. The symmetry of the metal-free macrocycle is however reduced to D_{2h} and the Q band splits into two distinct bands. The electronic spectrum of **1c** exhibited a Q-band at λ_{max} = 600 nm, which was however split into Q_x [λ_{max} = 558 nm] and Q_y [λ_{max} = 626 nm] in **1a** spectrum. This indicated that the Q-band shifted from D_{4h} in **1c** to D_{2h} symmetry in **1a** [16,17].

2,3,9,10,16,17,23,24-Octa substituted phthalocyanine (2a): ^{1}H NMR spectrum exhibited a signal with chemical shift 2.016 ppm characteristic of the pyrrolenine protons in the core [16]. The signals at 7.6-6.8 ppm were assigned to the benzyl protons. On the other hand its infrared spectrum exhibited a band at 3620 cm^{-1} assigned to the N-H stretching vibration [18]. The absence of the CN stretching band in the spectrum corroborated this further. It has been reported that the isoindole and pyrrole stretching frequencies serve as markers for phthalocyanine formation. This was observed at 1465-1378 cm^{-1} and 1321 cm^{-1} respectively [21-23]. Consequently they serve as further evidence for the formation of the macrocycle. Bands at 1250-1091 cm^{-1} and 1630-1229 cm^{-1} were assigned to isoindole and pyrrole breathing frequencies. Aromatic C=C and *ortho*-substituted benzene stretch was observed at 1582 cm^{-1} and 1700-1685 cm^{-1} respectively [18]. The ultraviolet-visible spectrum gave characteristic B-band at λ_{max}= 337 nm. In the visible region two intense absorptions of comparable intensity were observed. These are due to the splitting of Q-band into Q_x [λ_{max} = 666 nm] and Q_y [λ_{max} = 703 nm]. This therefore confirms the D_{2h} symmetry of **2a**. The transitions are assigned to $\pi \rightarrow \pi^*$ transitions. Signals at λ_{max} = 606 nm and λ_{max} = 639 nm were attributed to the sublevels within the Q_x and Q_y states [1,24,25].

Chromium complexes: The characterization of these compounds was achieved using elemental analyses, infrared and electronic spectroscopic techniques. Their spectral assignment was carried out by comparison of the spectrum of the free base, the complexes and that of similar compounds in literature [16,24]. Evidence for the formation of the complex **1b** was given by the absence of the N-H stretching band in the infrared spectrum of the complex [16,24], suggestive of the deprotonation of the pyrrole nitrogen atoms and indicative of coordination. This band was however observed at 3395 cm^{-1} for the free base **1a**. Further evidence for coordination of Cr(III) ion in the central cavity of **1a** was given by the hypsochromic shifts observed for the C-N and C-H stretching frequencies from 2929 and 1307 cm^{-1} in the ligand to 2939 and 1329 cm^{-1} in the complex respectively [19]. Appearance of a new band in the spectrum of **1b** at 550 cm^{-1} assigned to metal-nitrogen stretching frequency, further confirm the coordination of Cr(III) ion by **1a** [19,26].

Electronic spectra are generally useful for establishing the structure of porphyrazines and their complexes [16,24]. The electronic spectrum of ligand **1a** exhibited two intense bands at 548 and 626 nm (Fig. 1), characteristic of free base porphyrazine molecule assignable as Q bands [1]. After the formation of the complex **1b**, the Q bands appeared as a single band at 625 nm (Fig. 2) with a bathochromic shift indicating that the symmetry of the free ligand changed from D_{2h} to D_{4h}, typical of a porphyrazine complex. As a consequence, it serves as confirmation of coordination of Cr(III) within the core of **1a** [1-3,16,24]. A broad band observed in the spectrum of the complex at 482 nm was assigned to $^4A_{2g} \rightarrow {}^4T_{1g}$ transition, characteristic of a d^3 Cr(III) configuration, in agreement with previous studies [27]. A band at 557 nm was attributed to ligand charge transfer band (LMCT) $a_{1u} \rightarrow e_g(d)$ [11,12]. This band was however absent in the spectrum of the Cr(III) ion and that of the free base and therefore corroborated the coordination of Cr(III).

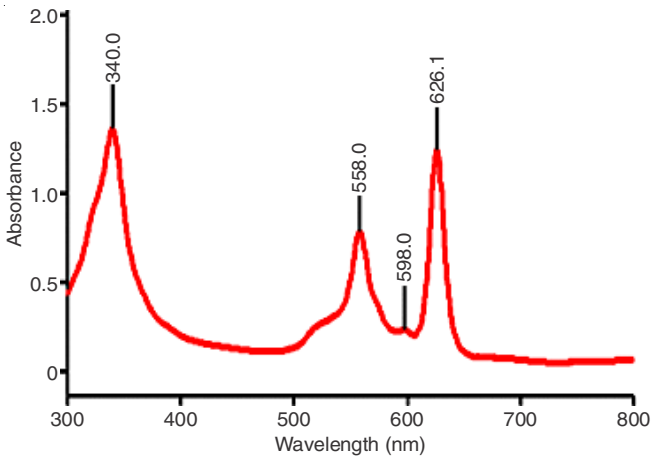


Fig. 1. UV-visible spectrum of compound **1a**

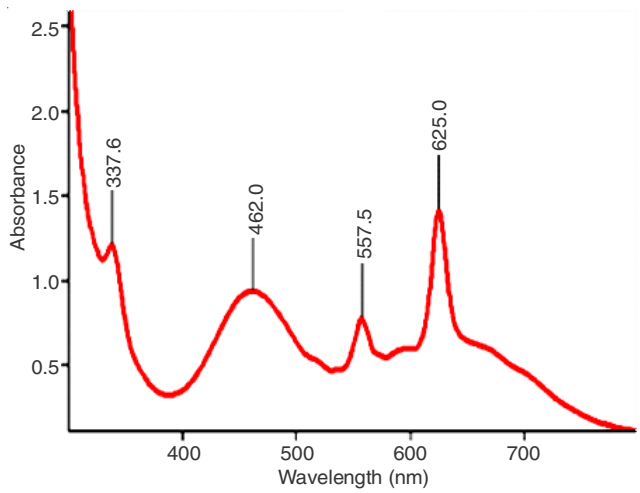


Fig. 2. UV-visible spectrum of compound **1b**

Similar to that obtained for the **1b** complex, absence of the N-H band in the infrared spectrum of the complex indicated complexation to obtain **2b** [16]. The C-N band gave a hypsochromic shift from 1342 to 1351 cm^{-1}. The electronic spectrum of free base **2a** exhibited two intense bands at 668 and 704 nm attributable to Q bands. On complexation, these gave a single band with a hypsochromic shift to 710 nm, diagnostic of coordinated tetrapyrroles and therefore suggested coordination of the Cr(III) ions with **2a** [1,28]. Further evidence for the coordination of Cr(III) to the free base ligand of **2a** was given by the appea-

rance of a broad band at 460 nm in the electronic spectrum of the complex which was absent in that of the ligand. This band was assigned to *d-d* transition, $^4A_{2g} \rightarrow {}^4T_{1g}$, for a d^3 configuration [27]. A weak band observed at 672 nm, was attributed to charge transfer band, thus coordination of Cr(III) by **2a** was confirmed [11].

Kinetic studies

Metalation: The rate of incorporation of Cr(III) into **1a** and **2a** was studied. Preliminary repetitive scanning of the ultraviolet spectral region during the reaction gave well defined isosbestic points (Figs. 3 and 4). Typical spectra changes for these reactions are presented in Figs. 3 and 4. The plots of 1/[A] *versus* time were linear, suggesting second order kinetics (Fig. 5).

The results obtained indicated that the rate of incorporation of Cr(III) into **1a** was faster than that of **2a**. From previous studies it is known that the nucleus of tetrapyrrole macrocycles deforms to enable effective coordination and this is a function of the peripheral substituents [13,29,30]. In this case the ligands used, phthalocyanine and porphyrazine derivatives have similar ring systems. As such they may be viewed as variants of each

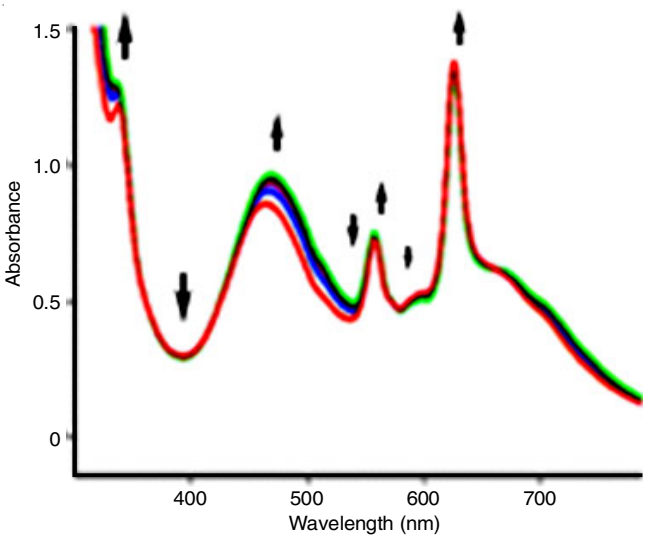


Fig. 3. Spectral changes for the metalation of **1a**

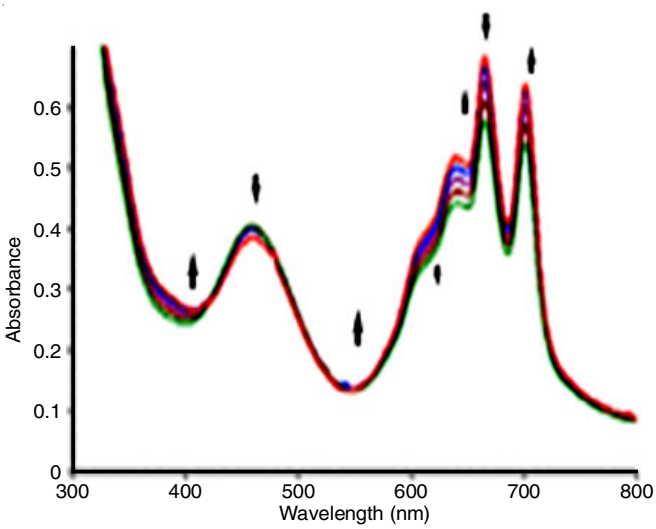


Fig. 4. Spectral changes for the metalation of **2a**

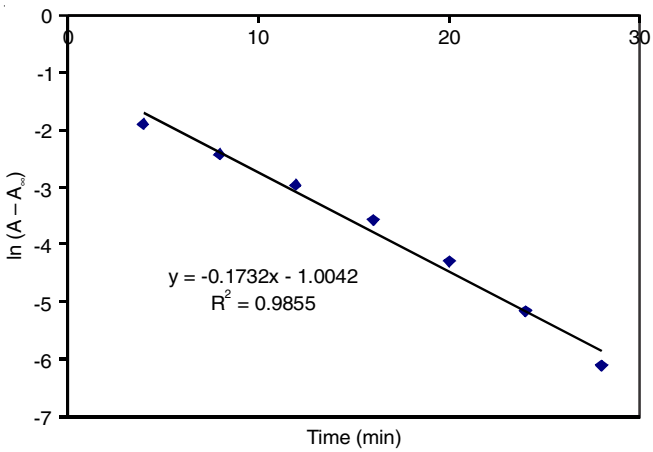


Fig. 5. A plot of ln (A–A∞) *vs.* time (min) at 25 °C for formation of **1b**

other with phthalocyanine a derivative of porphyrazine with the fused benzo group as a substituent [31-33]. Consequently the difference in the rate of insertion may be seen as the effect of the respective substituents attached to the ring system. It is suggested that the flexibility of the propyl substituents induces a form of flexibility on the core of **1a**. On the other hand the rigid benzo and phenoxy substituents on **2a** inhibits the deformation of the central cavity of **2a** resulting in the slower rate of incorporation of Cr(III) ions. These observations are in agreement with that obtained for previous studies [29,34].

The rate of incorporation of Cr(III) was however slower than that obtained for Cu(II) and Co(II) ions reported for similar ligands [13]. This is totally not unexpected and may be attributable to the kinetic inertness of chromium(III) ion. Ligand exchange and rearrangement reactions are generally slow for Cr(III) complexes and this may be ascribed to the stability of the half-filled t_{2g} energy level for an octahedral d^3 configuration for Cr(III). As a consequence these findings demonstrate the ability of tetrapyrrole macrocyclic compounds to selectively bind metals ions [30,35,36]. It is suggested therefore, that this is a function of the cavity size, nature of the peripheral substituents of the ligand as well as, the size, oxidation state and kinetic stability of the incoming metal ions.

The rate for incorporation of Cr(III) into the ligands increased with the increase in temperature. This trend was observed for all the reactions. This may be explained from previous studies, of Inada and co-workers [26]. They pointed out that distorting the highly conjugated π-system of these macrocycles requires a positive enthalpy change, leading to a large positive value of activation entropy due to the increase in the intra-molecular freedom of the stretching and bending modes of the macrocyclic ring [34].

Mechanism of metalation: Two potential pathways are proposed for the mechanism of incorporation of Cr(III) into **1a**. The first pathway involves the incorporation of the Cr(III) into the central cavity of the free base **1a**, obtained from the demetalation of the **1c**.

$$\mathbf{1a}_{\text{freebase}} + \text{Cr(III)} \longrightarrow \mathbf{1a}\text{-Cr(III)} \quad (1)$$

The second pathway represents the direct incorporation of chromium(III) ion into **1c** without obtaining the free base first (eqns. 2 and 3). It consists of at least two steps, the coordi-

nation of the Cr(III) complex with the ligand *via* the pyrrolenine nitrogen and the simultaneous coordination of Mg(II) *via* the two pyrrole nitrogen atoms to give the hetero-diuclear intermediate complex (Fig. 6). The second step being the dissociation of the magnesium ion and subsequent coordination of Cr(III) *via* the two pyrrole nitrogen atoms [30,35,36].

$$\text{Mg(II)-}\mathbf{1a} + \text{Cr(III)} \longrightarrow \text{Mg(II)-}\mathbf{1a}\text{-Cr(III)} \quad (2)$$

$$\text{Mg(II)}\mathbf{1a}\text{-Cr(III)} \longrightarrow \text{Cr(III)-}\mathbf{1a} + \text{Mg(II)} \quad (3)$$

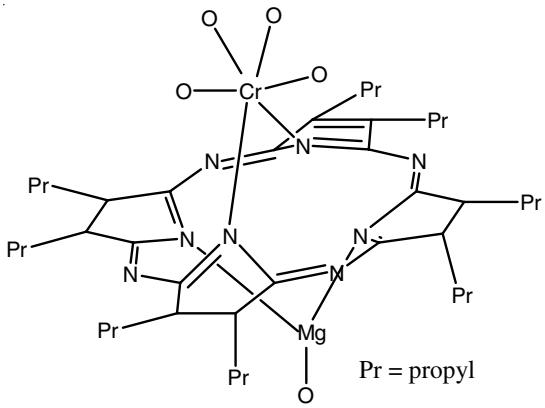


Fig. 6. Heterodinuclear complex

There was no significant difference in the rate of incorporation or Cr(III) *via* both pathways (Table-1). This was further supported by the activation energy of formation for both reaction pathways in which there was no significant difference (Table-1). This indicates that the demetalation of **1c** is not a pre-requisite for the incorporation of Cr(III) ion into the central cavity of **1a**. These findings are in accord with those proposed by Hambright and Chock [37]. It is however, not consistent with those obtained by Isabirye *et al.* [13] for previous studies using similar ligands with divalent metal ions. This discrepancy implies that the mechanism of incorporation of transition metal ions into the central cavity of **1a** is a function of the kinetic inertness and size of the metal ions.

TABLE-1
RATE CONSTANT (K, 25.0 °C) AND ACTIVATION ENERGY (E_a) FOR THE KINETIC REACTIONS

Comp.	Metalation		Redox reaction	
	K (M^{-1} s^{-1})	E_a (KJ mol^{-1})	K (M^{-1} s^{-1})	E_a (KJ mol^{-1})
1b	0.1732	58.47	0.0691	39.13
1c	0.1677	58.57		
2b	0.0855	28.53		

Redox activity: The redox reaction involving complexes **1b** and **1d** was studied (Table-1, Fig. 7). The plots of 1/[A] *versus* time were linear, which suggested that the reactions followed second order kinetics. Confirmation of the spectral assignments for the spectrum obtained during the redox reaction involving Cr(III) **1a** and Co(II) **1a** was achieved by comparing the electronic spectra of the complex (Fig. 3) and that observed of the redox reaction (Fig. 7). The observed spectral changes during the redox process showed that the Q-band shifted hypsochromically from 625 to 629 nm, with increase in intensity. On the other hand, the B band observed at 337 nm gave a blue

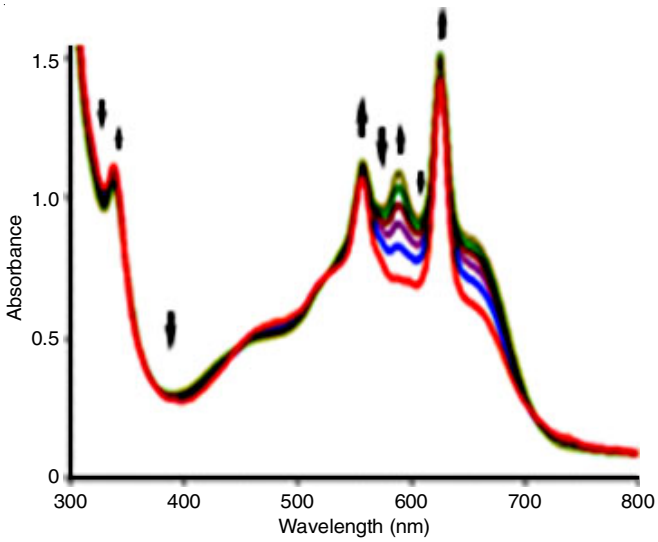


Fig. 7. Spectral changes for the reduction of **1b**

shift to 333 nm. These spectral variations suggest that the redox process only weakly affected the macrocyclic π system of Cr(III) **1a**. Similar minor changes have been reported for redox processes involving porphyrins and porphyrazines [38]. Clear isosbestic points were obtained at 586, 516 and 660 nm (Fig. 7) indicating the lack of any spectrally detectable intermediates [28,38]. In addition the spectrum for the redox reaction showed the complete disappearance of the broad band at 462 nm attributed to the *d-d* transition for a d^3 Cr(III) system and the appearance of a new weak band at 590 nm. No shift was observed for the charge transfer band $a_{1u} \rightarrow e_g(d)$, at 557 nm, that however increased in intensity [11,12]. It is suggested that the concomitant disappearance of the *d-d* transition band of Cr(III), reappearance of the LMCT band and appearance of a weak new band is indicative of changes in the energy and population of the Cr(III) ion orbitals. This is supported by Lever and co-workers [11], who showed that the reappearance of this LMCT serves as an indication of the reduction of Cr(III) to Cr(II). As a consequence, it is proposed that the electron transfer reaction for both complexes was metal based, with Co(II) serving as the electron donor and Cr(III) the acceptor, (eqns. 4-5). The result obtained is in agreement with previous reports in which the first redox step for complexes with redox active metal ions is metal based [1-3,9,11,12,38].

$$\text{Cr(III)}\mathbf{1a} + e^- \longrightarrow \text{Cr(II)}\mathbf{1a} \quad (4)$$

$$\text{Co(II)}\mathbf{1a} \longrightarrow \text{Co(III)}\mathbf{1a} + e^- \quad (5)$$

Conclusion

It can be concluded from the study that although the rate of incorporation of metal ions within the central cavity of tetrapyrrole macrocyclic compounds are a function of their peripheral functionalities and the size of the metal ions, it is also dependent on the inertness of the metal ion. This study also showed that the cost effective pathway for incorporation of Cr(III) ion for the porphyrazine ligand is the direct insertion of the metal ion into the magnesium porphyrazine complex with the formation of the hetero-dinuclear complex. Metal-based redox activity was established for the Cr(III) porphyrazine complex.

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